Phenyl-γ-(2-pyridyl)-propylcarbinol.—Into a 3-necked flask, equipped with stirrer, dropping funnel, reflux condenser and calcium chloride tubes protecting each opening, and containing 0.015 mole of lithium aluminum hydride (in dry ether), was added 7 g. (0.03 mole) of phenyl γ-(2-pyridyl)-propyl ketone in 20 ml. of ether at a rate just fast enough to produce gentle boiling. The excess lithium aluminum hydride and the organo-metallic complex were decomposed by the addition of moist ether. After the precipitate of aluminum hydroxide and lithium hydroxide had been filtered off and the ether solution had been dried over Drierite, the ether was evaporated under reduced pressure, leaving 6 g. of a pale yellow solid, m. p. 65–67°. After four recrystallizations from hexane there was obtained 3.8 g. (54%) of beautiful clusters of white needles, m. p. 66.5–67°.

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.26; H, 7.54. Found: C, 78.93; H, 7.37.

The **picrate** of phenyl-γ-(2-pyridyl)-propylcarbinol was obtained from alcohol as clusters of yellow needles, m. p. 112.5–114°.

Anal. Calcd. for $C_{21}H_{20}N_4O_7$: C, 55.26; H, 4.42. Found: C, 55.49; H, 4.43.

Summary

In an effort to obtain model compounds of possible relationship to β-erythroidine the synthesis of certain lactones derived from quinolizidine has been investigated. In the course of this work a new compound, phenyl-γ-(2-pyridyl)-propylcarbinol, having a central action in effecting muscular paralysis was discovered.

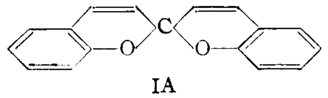
ROCHESTER, NEW YORK RECEIVED MARCH 24, 1950

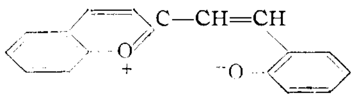
[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

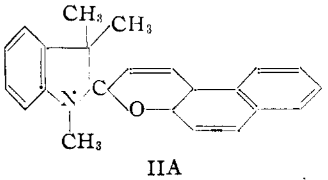
Structure and Polarity of Some Polycyclic Spirans

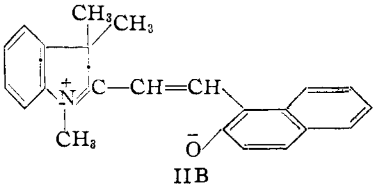
BY ERNST D. BERGMANN, ANNA WEIZMANN AND ERNST FISCHER

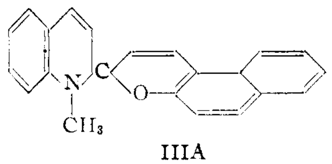
Certain polycyclic spirans show the effect of thermochromy. Thus 1,3,3-trimethylindolino-β-naphthopyrylospiran (II) is a colorless substance, but its melt is blue, and its solutions in non-polar solvents, which are pink at room temperature, turn intensely red upon heating. The phenomenon is reversible and has been interpreted as being due to variation in the contribution of the polar (colored) mesomeric structure (IIB).[1,2] The colorless dibenzospiropyran (I) does not show the above phenomenon. It is, therefore, assumed that a possible polar form (IB) does not contribute to the structure of this molecule under the experimental conditions employed.

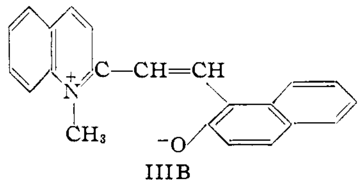

IA

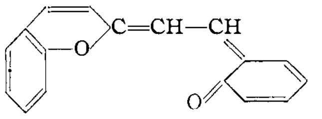

IB

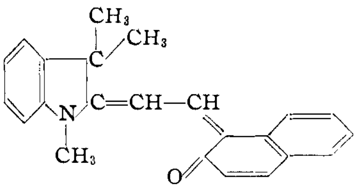

IIA

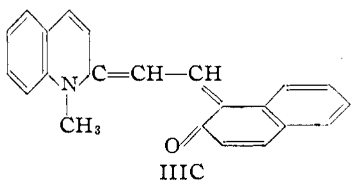

IIB


IIIA


IIIB


IC


IIC


IIIC

On the other hand, N-methylquinolino-β-naphthopyrylospiran (III) is blue-green even in

---

[1] Loewenbein and Katz, *Ber.*, **59**, 1377 (1926); Dilthey and co-workers, *Ber.*, **59**, 1856 (1926); **61**, 963 (1928); *J. prakt. Chem.*, [2] **114**, 179 (1926); Heilbron and co-workers, *J. Chem. Soc.*, 1699 (1927); 2077 (1928); 936 (1929); 1336 (1931); 430, 1263 (1933); 1571 (1934); 1380 (1936).

[2] Wizinger and Wenning, *Helv. Chim. Acta*, **23**, 247 (1940).

the solid state, and its solutions in non-polar solvents at room temperature are very intensely blue. The contribution of the polar structure (IIIB) should, therefore, be considerable.[2]

It was to be expected that compound (III) would have a higher dipole moment than (I) or (II). Measurements at 30° have verified this conclusion

I	1.20 ± 0.02 *D* (in benzene)
II	1.38 ± 0.02 *D* (in benzene)
	1.43 ± 0.02 *D* (in toluene)
III	7.9 ± 0.2 *D* (in α-methylnaphthalene)
	10.4 ± 0.5 *D* (in benzene)

The dipole moments found for (I) and (II) are in reasonable accord with the values calculated for non-polar structures.[3] Equally, the assumption of a considerable contribution of a polar structure in the molecule of (III) seems to be justified and is well in keeping with the large moments found recently for somewhat similar compounds of the merocyanine type.[4] One might further expect that the moment of (II) should increase with temperature, parallel to the increase in color intensity. However, in toluene solution at 90°, a value of only 1.52 ± 0.02 *D* was observed, as compared with 1.43 ± 0.02 *D* at 30°. This would seem a very small increase for any significant contribution of a polar structure such as (IIB); on the other hand, the color change is marked, although the absolute color intensity of solutions of (II) at 90° is fairly small, if compared with the color of (III). It is perhaps necessary to assume that color may not only be due to structures like (IB), (IIB), (IIIB), but also to quinoid non-spiranic and non-ionic forms such as (IC), (IIC), (IIIC), in accordance with a suggestion offered by Hukins and Le Fèvre (ref. 3). As such forms can be expected to have smaller moments than the zwitterions (IB), (IIB), (IIIB), this hypothesis could explain color change without accompanying rise in electric moment. It does not explain, however, why the contribution of the various forms to the actual state of the molecule, varies from compound to compound.[5]

The difference observed for the moments of (III) in benzene and α-methylnaphthalene, respectively, is unduly large, but may perhaps, at least partly, be ascribed to the following two effects.

(a) In general, the orientation polarization of substances in solution decreases with increasing dielectric constant of the solvent.[6] Indeed, for 4-bromonitrobenzene,[7] moments of 2.68 *D* and 2.47 *D* have been observed in benzene and in α-methylnaphthalene, respectively, in this laboratory.

(b) It was found that solutions of (III) in α-methylnaphthalene gradually lose their color. This may be due to a reaction of (III) with the solvent or with an unknown impurity of the latter. Although this effect develops slowly, it may account to a certain extent for the lower value of the moment found in α-methylnaphthalene solution.

Experimental

(a) Substances. Dibenzospiropyran (I).—Disalicylideneacetone was prepared[8] from 20 g. of salicylaldehyde, 4.8 g. of acetone and 80 ml. of 4 *N* sodium hydroxide solution at room temperature (fifteen hours). The reaction mixture was filtered, and the green precipitate dissolved in 500 ml. of water, and, after filtration, treated with 5% hydrochloric acid. The precipitate (15 g.) crystallized from a benzene–alcohol mixture (5:1) in cream-colored needles, m. p. 168° (dec.). *Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.4; H, 5.6. The conversion into (I) was best effected by heating of 1-g. portions at 157–160° for five minutes with stirring.[9] Sublimation under 0.2 mm. pressure at 160–180° gave a product of m. p. 100–102°. *Anal.* Calcd. for $C_{17}H_{12}O_2$: C, 82.3; H, 4.9. Found: C, 82.0; H, 5.1.

1,3,3-Trimethylindolino-β-naphthopyrylospiran (II).[2]—The methylphenylhydrazone of methyl isopropyl ketone (11.5 g.) was treated for six hours at room temperature with a solution of 34.5 g. of zinc chloride in 30 ml. of anhydrous alcohol. The zinc compound was filtered, washed with ether and decomposed with 10% potassium hydroxide solution. The resultant 2-methylene-1,3,3-trimethylindoline ("Fischer's base") was extracted with ether; yield, 2.2 g., m. p. of the picrate 148°.[10] (II) was obtained from the base and 2-hydroxy-1-naphthaldehyde in boiling methanol. It crystallized from light petroleum in white crystals, m. p. 182–183° (blue melt); yield 2.3 g.

N-Methylquinolino-β-naphthopyrylospiran (III).[2]—Using 50 ml. of boiling ethanol as solvent, 8.1 g. of quinaldinium methosulfate (m. p. 140–145°) was condensed with 5.1 g. of 2-hydroxy-1-naphthaldehyde by means of ten drops of piperidine. After fifteen minutes, 60% perchloric acid was added until the color had turned orange. The N-methyl-2-(2′-hydroxy-1′-naphthylidene)-quinaldinium perchlorate so obtained (from pyridine, m. p. 258–260°; 2.2 g.) was heated with an excess of aqueous ammonia at 100° for two hours. The solid product (1.7 g.) was recrystallized from pyridine to give green crystals, m. p. 232–233°.

(b) Methods.—The measurements were carried out in a Sayce–Biscoe cell of 56 *p*F air capacity. The cell was immersed in an oil-bath thermostated to ±0.02°. A heterodyne beat apparatus described by Chien[11] was applied. A General Radio Co. type 722-D instrument served as precision measuring condenser.

The computation of the molar polarization and the molar refraction at infinite dilution, described by Le Fèvre,[12] was

---

(3) It should be noted that in the case of compound (I) and similar symmetric compounds a possible contribution of polar structures in which the two oxygens acquire positive and negative charges, respectively, should not result in a finite dipole moment, since the moments of the two equally probable structures represented schematically by $O^+\ldots\ldots O^-$ and $O^-\ldots\ldots O^+$, would cancel each other. The same applies also to substances of the benzo-β-naphthobis-*spiro*-2-pyran and di-β-naphthobis-*spiro*-2-pyran type, for which Hukins and Le Fèvre (*J. Chem. Soc.*, 2088 (1949)) found moments of the order of magnitude of 1.5, unaffected by the temperature and the corresponding development of color. (The paper of the British authors appeared after the present investigation had been completed.)

(4) Kushner and Smyth, This Journal, **71**, 1401 (1949).

(5) This discussion is based on a suggestion made by one of the Referees, which is gratefully acknowledged by the authors.

(6) Mueller, *Trans. Faraday Soc.*, **30**, 731 (1934).

(7) Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931), reports a moment of 2.65 for this compound.

(8) Fabinyi, German Patent 110,521 (1898); *Chem. Zentr.*, **71**, II, 302 (1900).

(9) Decker and Felser, *Ber.*, **41**, 2997 (1908).

(10) Brunner, *ibid.*, **31**, 612 (1898).

(11) Chien, *J. Chem. Education*, **24**, 494 (1947).

(12) Le Fèvre, "Dipole Moments," Methuen, London, 1948.

employed. No corrections for solvent polarization[13] had to be introduced. The densities were measured in a bicapillary pycnometer of about 7 ml. capacity. The molar refractions were both measured experimentally and calculated from bond refraction data,[14] and the average between the two values was used in the computation of the dipole moments. For compound (III), only the calculated molar refraction was employed.

TABLE I

MEASURED DIELECTRIC CONSTANTS, REFRACTIVE INDICES AND DENSITIES OF SOLVENTS USED

Solvent	Dielectric constant	Refractive index	Density
Benzene at 30°	2.262	1.4942	0.86793
Toluene at 30°	2.360		.85751
Toluene at 90°	2.237		.79725
α-Methylnaphthalene at 30°	2.794	1.6100	1.0124

TABLE II

DIELECTRIC CONSTANTS, REFRACTIVE INDICES, AND DENSITIES OF SOLUTIONS

Compound I in benzene at 30°

$w10^4$	$\Delta\epsilon 10^4$	$\Delta n^2 10^4$	$\Delta d 10^5$
0	−1	0	2
32	30	...	..
60	56	...	..
86	81	...	..
115	108	42	..
145	136	...	..
176	164	81	..
208	194	...	..
248	228	...	..
310	...	...	801
658	...	248	1709

Compound II in benzene at 30°

$w10^4$	$\Delta\epsilon 10^4$	$\Delta n^2 10^4$	$\Delta d 10^5$
0	−3	2	5
77	79	33	..
90	94	...	196
98	102	42	..
108	111	...	..
120	123	51	300

Compound II in toluene at 30°

$w10^4$	$\Delta\epsilon 10^4$	$\Delta d 10^5$
0	−2	3
19	18	...
36	35	...
52	49	...
72	69	...
92	88	...
110	104	...
128	123	293
400	...	924

Compound II in toluene at 90°

$w10^4$	$\Delta\epsilon 10^4$	$\Delta d 10^5$
0	8	7
45	37	...
67	53	...
93	74	...
116	93	...
136	110	...
158	127	...
178	143	385
400	...	856

Compound III in benzene

$w10^4$	$\Delta\epsilon 10^4$
0	−3
0.11	6
.21	8
.36	12
.47	19
.55	23
.67	25
.78	27

Compound III in α-methylnaphthalene

$w10^4$	$\Delta\epsilon 10^4$
0	−5
0.60	17
1.14	35
1.54	50
2.21	71
2.75	97
3.49	106
3.95	121
4.43	137

Results

The dielectric constants ϵ, the squares of the refractive indices n^2, and the densities d, of the solutions were found to be linear functions of the weight fraction w, according to the equations $\epsilon = \epsilon_0 (1 + \alpha w)$; $n^2 = n^2_0 (1 + \gamma w)$; $d = d_0 (1 + \beta w)$. The respective values, ϵ_0, n^2_0, d_0, for the pure solvent, found by extrapolation from the experimental lines to zero concentration, agree reasonably well with the values measured directly. From the values of α, β, γ, found from the slope of the experimental lines, the molar polarizations, P_∞, and the molar refractions, R_∞, at infinite dilution were calculated according to the equations

$$P_\infty = M[p_0(1 - \beta) + C\alpha\epsilon_0]$$
$$R_\infty = M[r_0(1 - \beta) + C'\gamma n_0^2]$$

where M is the molecular weight of the solute, p_0 and r_0 are the specific polarization and refraction of the solvent

$$C = \frac{3}{(\epsilon_0 + 2)^2 d_0}$$
$$C' = \frac{3}{(n_0^2 + 2)^2 d_0}$$

The dipole moments were obtained from the usual equation

$$\mu = 0.128[(P_\infty - R)T]^{1/2}$$

The data for the solvents used are recorded in Table I.

The results are summarized in Tables II and III. Here $\Delta\epsilon$, Δn^2 and Δd are defined by $\Delta_\epsilon = \epsilon - \epsilon_0$; $\Delta n^2 = n^2 - n_0^2$; $\Delta d = d - d_0$. They were measured with an accuracy of ±0.0002, ±0.0004 and ±0.00003, respectively. R_D denotes the molecular refraction calculated from bond-refraction data.

TABLE III

EMPIRICAL CONSTANTS, POLARIZATIONS, REFRACTIONS AND DIPOLE MOMENTS

Solute	Solvent	Temp., °C.	$\alpha\epsilon_0$	β	γn_0^2	P_∞	R_∞	R_D	$^1/_2(R_D + R_\infty)$	P_0	μ
I	Benzene	30	0.930	0.299	0.378	103.7	76.1	73.7	74.9	28.8	1.20 ± 0.02
II	Benzene	30	1.007	.288	.426	141.8	104.2	103.1	103.6	38.2	1.38 ± 0.02
II	Toluene	30	0.959	.269	...	145.0	...	...	(103.6)	41.4	1.43 ± 0.02
II	Toluene	90	.800	.268	...	142.3	...	...	(103.6)	38.7	1.52 ± 0.02
III	Benzene	30	37.5	(.29)[a]	...	2295	...	97	.....	2198	10.4 ± 0.5
III	α-Methylnaphthalene	30	30.8	(.08)[a]	...	1342	...	97	.....	1245	7.9 ± 0.2

[a] These values were calculated, using the assumption that II and III possess equal molar volumes.

---

(13) Kumler and Halverstadt, THIS JOURNAL, **64**, 2988 (1942).

(14) Denbigh, *Trans. Faraday Soc.*, **36**, 926 (1940).

For 4-bromonitrobenzene, only the final data are recorded here:

Solvent	Temp., °C.	$\alpha_{\epsilon 0}$	β	P_∞	R_D	P_0	μ
Benzene	30	3.96	0.511	186.2	40.7	145.5	2.68 ± 0.02
α-Methylnaphthalene	30	4.64	.413	164.3	40.7	123.6	2.47 ± .02

Summary

The dipole moments of three polycyclic spirans have been measured. The high moment found for the intensely colored (III) bears out the assumption that a zwitterionic structure (IIIB) contributes considerably to the actual state of this molecule. The slightly colored, thermochromic (II) has a comparatively small moment of the same order of magnitude as that of the colorless, non-thermochromic (I). As this moment does not increase appreciably with the temperature, parallel to the appearance of color, it is suggested that color may be due not only to zwitterionic structures (IB), (IIB), (IIIB), but also to non-zwitterionic, non-spiranic, quinoid forms such as (IIC).

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL
RECEIVED NOVEMBER 26, 1949

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Aryltrichloromethylcarbinols

BY ERNST D. BERGMANN, DAVID GINSBURG AND DAVID LAVIE[1]

In a previous paper,[2] the condensation of ketones and branched-chain aliphatic aldehydes with chloroform has been investigated, using potassium hydroxide as the condensing agent, in conjunction with acetals as the reaction medium. This reaction has now been extended into the series of benzaldehyde and its substitution products (Table I).

Several workers[3,4,5,6] have previously condensed *benzaldehyde* with chloroform in the presence of small quantities of powdered potassium hydroxide; Howard[4] obtained a yield of 16% of phenyltrichloromethylcarbinol when he used 18% of the molar quantity of potassium hydroxide. Evidently, his experiments were carried out under the assumption that alkali serves as a catalyst—while experience has shown that not a free trichloromethylcarbinol is formed in this type of reaction, but its potassio derivative. The influence of increased quantities of the hydroxide on the conversion was therefore investigated. An amount of 36% of the theory of potassium hydroxide gave, indeed, a yield of 30%, the remainder of the reactants being recovered. Increase of the alkali to the theoretical amount, however, gave only a yield of 41.3%, because of a side reaction which became marked under these conditions, leading to benzoic acid, 11% of the latter being isolated. The use of acetaldehyde-dibutylacetal as reaction medium was not advantageous, 25% of the chlorinated alcohol and 27.8% of benzoic acid being formed when one mole of potassium hydroxide was employed. In the case of 4- and 2-nitrobenzaldehyde, no condensation product was isolated at all, the only reaction taking place being the Cannizzaro condensation: the nitrobenzoic acids and nitrobenzyl alcohols were isolated. 2-Phenylbenzaldehyde behaved likewise.

In view of the negligible effect of the presence of acetals on the condensation between benzaldehyde and chloroform, the systematic study of the reaction between the latter and the substituted benzaldehydes which are listed in Table I was carried out without solvent but, in all cases, one mole of powdered potassium hydroxide was used for each mole of aldehyde. All aldehydes gave the expected reaction and, as far as they are concerned, no significant differences in the influence of methyl, chloro and methoxy groups, respectively, is visible, nor does the position of the substituent (*o*, *m*, *p*) have a marked effect. In particular, substituents in the ortho position do not appear to cause an effect describable as steric hindrance. In the reaction with 3-chlorobenzaldehyde, a substantial amount of 3-chlorobenzoic acid was observed, which accounts for the low yield of (3-chlorophenyl)-trichloromethylcarbinol (12%). In all other cases in Table I, the amount of acid formed (*i. e.*, the extent to which Cannizzaro reaction occurred) was relatively small.

All the carbinols were slowly-crystallizing liquids, but their acetates were well-defined, crystalline solids.

It has been shown recently[7] that substances of the type $RCHOHCCl_3$ can be transformed into α-alkoxy-acids according to the equation

$$RCHOHCCl_3 + R'OH \xrightarrow{KOH} RCH(OR')COOK$$

---

[1] Some of the experimental work described in this paper forms part of a thesis presented by D. Lavie to the Hebrew University in partial fulfilment of the requirements for the degree of Ph.D.

[2] Ch. Weizmann, E. Bergmann and Sulzbacher, THIS JOURNAL, **70**, 1189 (1948).

[3] Jocicz, *Chem. Zentr.*, **68**, I, 1013 (1897).

[4] Howard, *et al.*, THIS JOURNAL, **47**, 455 (1925); **57**, 376, 2317 (1935).

[5] Rapson, Saunder and Steward, *J. Chem. Soc.*, 74 (1944).

[6] von Leuthold, French Patent 791,172 (*C. A.*, **30**, 3157 (1936)).

[7] Ch. Weizmann, Sulzbacher and E. Bergmann, THIS JOURNAL, **70**, 1153 (1948).